# ELECTRON PARAMAGNETIC RESONANCE SPECTRUM OF LIQUID OXYGEN DIFLUORIDE[1]

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## INTRODUCTION

The electron paramagnetic resonance spectrum of liquid oxygen difluoride has been determined in conjunction with a study of the structure of liquid inorganic oxidizers. Pure liquid $OF_2$ exhibited no EPR signal when condensed in the absence of light. Upon photolysis, a strong doublet with a hyperfine splitting of 13.5 gauss and a g-value of 2.0036 was obtained. Concentrations were on the order of $10^{16}$ unpaired electrons per sample. Oxygen difluoride is a colorless gas at room temperature, and a pale yellow liquid below 128°K, its normal boiling point. It is relatively stable, with thermal decomposition beginning at about 200 - 250°C. $OF_2$ is nonlinear, with two equivalent O-F bonds having an FOF angle of angle of 104°.

## EXPERIMENTAL

### Electron Paramagnetic Resonance

EPR measurements were made using a Varian V-4502 X-band spectrometer equipped with a 6 in magnet and using 100 kc field modulation. Frequencies used were of the order of 9.1 Gc. The sample tube was a 3.0 mm I.D. quartz tube connected to a stopcock and a male ground glass joint by means of a graded seal. Sample volumes were of the order of 0.05 ml. For measurements at 77°K, the sample tube was placed in a small quartz dewar which was inserted into the cavity. Measurements in the range from 88°K to 138°K were made using a V-4557 variable temperature accessory. Peroxylamine disulfonate in a capillary affixed to the outside of the dewar was used for the scan calibration and as a standard for the g-value determination. The total width of the peroxylamine disulfonate spectrum was taken to be 26.0 gauss and the g-value used was 2.0055 (2). The frequency was determined with a Hewlett-Packard Model X-532B wavemeter. The g-value of polycrystalline DPPH was determined as a check on the procedure. Concentration measurements were made relative to a Varian 0.1 per cent pitch sample in KCl, with the number of spins taken to be $3 \times 10^{+15}$ spins/cm length of sample. The accuracy of this value is estimated to be $\pm 25\%$ (3). However, we are more interested in relative values of the intensities of the $OF_2$ spectra at various temperatures (compared with the same pitch standard) than we are in absolute values of the spin concentrations.

Photolysis studies were performed using a PEK-110 100 watt high pressure mercury arc lamp. The 3660 angstrom line was selected by means of a Bausch and Lomb second order interference filter.

## Purification

The $OF_2$ was bled slowly from the storage tank through an HF trap and condensed on the cold vertical column. The HF trap removed hydrogen fluoride and silicon tetrafluoride (4), while the cold column separated any carbon dioxide present. This vertical column was at 77°K and jacketed with a dewar. The $OF_2$ condensed and drained below the cold region of the tube where it refluxed and slowly distilled into the first liquid nitrogen trap. Following Schoenfelder's procedure for $N_2F_4$ (5), the $OF_2$ was chromatographed. Table I shows the relative elution times of the impurities found to be present. Prior to the introduction of the helium carrier gas, it was passed through reduced copper oxide wire at 500°C (6) to remove oxygen and Linde molecular sieve to remove $H_2O$.

TABLE I

RELATIVE ELUTION TIMES ON $\frac{1}{2}$" x 10' SILICA GEL COLUMN,
FLOW RATE, 150 ml/min

| Substance | Elution Time of Maximum (min) |
|-----------|-------------------------------|
| $O_2$     | 4.7    |
| $N_2$     | 5.1    |
| $OF_2$    | 10.8   |
| $F_2$     | 13.0   |
| $CF_4$    | 16.5   |
| $CO_2$    | 120.0  |
| $SiF_4$   | >120.0 |

## Chemicals

The copper oxide wire was Mallinckrodt reagent grade. The molecular sieve was Linde 5A 1/16-in pellets. The $OF_2$ was obtained from Allied Chemical Corporation and was approximately 93 per cent pure. The silica gel (60/80 mesh) was purchased from Matheson Company.

## RESULTS

No EPR signal was obtained on samples of liquid $OF_2$ prepared in the absence of light. Liquid $OF_2$ taken directly from the tank in the presence of room light showed a fairly strong, complex signal with a total linewidth of about 100 gauss. Similar results were obtained from $OF_2$ which had been swept through an HF trap and subsequently distilled.

A sample of chromatographed liquid $OF_2$, prepared in the absence of light, showed a strong doublet (Fig. 1) with a splitting of 13.5 gauss when photolyzed. The linewidth is temperature dependent with values in the range of 1.6 - 3.6 gauss. The line center of the doublet has a g-value of 2.0036 ± 0.0003. The line shape

closely approximated a Lorentzian curve. The spectra were examined at various modulation amplitudes and microwave power levels in order to ensure that no distortion due to overmodulation or power saturation occurred. The intensity of the doublet increased with time during photolysis. The concentration of paramagnetic species was calculated to be on the order of $10^{16}$ unpaired electrons per sample, corresponding to a concentration of about 0.001 mole per cent. An EPR spectrum of chromatographed liquid $OF_2$ prepared in normal room light was the same as that obtained from the photolyzed samples.

The change of the signal intensity with photolysis is shown in Fig. 2 for a number of temperatures. The rate of formation of the radical species increased with temperature. The signal intensity behavior after photolysis was strongly temperature dependent. At 77°K the signal strength increased rapidly after the lamp was turned off, then more slowly. At intermediate temperatures, 87°K, 100°K, and 105°K; the intensity leveled off after photolysis. The curves fall off more rapidly at 121°K in the absence of light. The decay at 77°K did not proceed to zero intensity, but usually reached a value which persisted even after several days storage of the sample in the dark. The signal may be caused to vanish, or at least reach a very low level by vaporization and recondensation of the sample in the absence of light.

Figure 3 shows the signal strength as a function of continued photolysis at 77°K. A peak concentration was reached at about 10 min photolysis, after which time additional photolysis produced a diminution of the signal. At $24\frac{1}{2}$ min, the signal strength corresponded to approximately $10^{12}$ unpaired electrons. After the lamp was extinguished, the concentration immediately increased to a value on the order of $5 \times 10^{13}$ unpaired electrons. The concentration continued to increase in the absence of light. If the sample was irradiated again, the signal level rapidly dropped to the previous low value.

In general, the intensity of the EPR resonance increased with continued photolysis, reached a maximum, and dropped to a very low level. The intensity at the maximum was temperature dependent. In a series of experiments, spectra of $OF_2$ were taken during $7\frac{1}{2}$ min of photolysis and afterwards in the absence of light for sufficient time to observe trends in the signal intensity. The rate of formation increased with temperature. After the photolysis lamp was turned off, the intensity increased, leveled off gradually, or decreased more rapidly, depending on the temperature.

The effect of the presence of oxygen on the results of these experiments is difficult to assess at this time. However, since it is possible that oxygen may alter the mechanism of the photolytic reactions, or may broaden the EPR signal, rigorous measures described above were undertaken to affect its removal.

## DISCUSSION

The lack of an EPR signal in the spectra of samples chromatographed in the absence of light is strong evidence that liquid $OF_2$ is not paramagnetic. In addition, one would expect a hyperfine triplet from a paramagnetic species such as $OF_2\cdot$,

rather than the observed doublet. Considering the system involved, a doublet could arise from $O_xF\cdot$ or $F\cdot$ radicals, due to hyperfine interaction with a fluorine nucleus which has a spin of $\frac{1}{2}$. However, it is to be expected that the fluorine atom would react (to form $F_2$) much more rapidly than would the $O_xF\cdot$ radical. The fluorine radical has not been observed in the condensed phase, but has ben observed in the gas phase as six well-spaced resonances with a g-value of $4/3$. At a frequency of 9.249 Gc, 4,159 gauss was the lowest value of the magnetic field at which a resonance occurred (7).

We have studied the EPR of liquid $F_2$ at 77°K. Tank fluorine and fluorine run through an HF trap and distilled have exhibited a weak signal with a linewidth of about 75 gauss and a g-value near 2.0. The signal strength increased with photolysis and seemed to broaden. It is probable that the observed resonance in liquid fluorine was due to impurities. Present efforts to chromatograph liquid fluorine are being made more difficult by the high vapor pressure (280 mm Hg) of $F_2$ at 77°K.

The small value of the coupling constant in $OF_2$ (13.5 gauss) is not what one would expect from hyperfine interaction of an electron with a fluorine radical. As a comparison, the hyperfine splitting due to two equivalent fluorine nuclei in liquid $NF_2\cdot$ is 64 $^+_-2$ gauss (8). The hyperfine interaction due to a fluorine radical should be large, since the value calculated by assuming that the unpaired electron was wholly in the 2s orbital of the fluorine atom is 17,050 gauss (9). From a consideration of the above arguments, it is quite probable that the unpaired electron species observed in the present study is $O_xF\cdot$, and not $F\cdot$.

The EPR spectra of the higher oxygen fluorides ($O_2F_2$, $O_3F_2$, and $O_4F_2$) have been studied by Kirshenbaum and Grosse (10). They have observed two EPR signals from samples of $O_2F_2$ at 77°K. The resonances were assigned to the presence of intermediates in the decomposition $O_2F_2 \longrightarrow O_2 + F_2$ rather than to $O_2$, $F_2$, or $O_2F_2$ itself. The stronger of the two signals has been interpreted in terms of the presence of a radical with one unpaired electron, having a hyperfine interaction with only one fluorine nucleus. $O_2F\cdot$ was considered to be a likely possibility. The weaker resonance is associated with the presence of a radical in the triplet state.
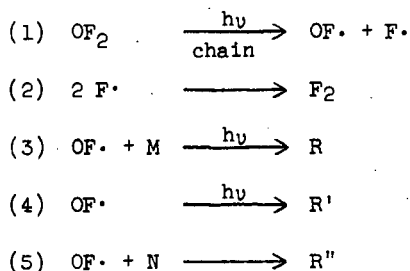
The EPR spectrum of $O_3F_2$ showed (10) the same resonances as were obtained from $O_2F_2$, except that the intensity of the stronger signal in the case of $O_3F_2$ was 50 - 100 times greater than the intensity of the corresponding resonance in $O_2F_2$, while the triplet resonance in $O_3F_2$ is only twice as intense as the triplet resonance in $O_2F_2$. The strong signal in $O_3F_2$ was also assigned to the $O_2F\cdot$ radical. Contamination of the $O_2F_2$ with $O_3F_2$ was ruled out by the observation of the resonances after the $O_2F_2$ sample had been heated above the decomposition temperature of $O_3F_2$.

$O_4F_2$ was found to be paramagnetic (10). The EPR spectrum at 77°K consisted of a strong doublet with an average g-value of 2.009 and a doublet separation on the order of 13 gauss. In view of the dissimilarity between the spectrum of $O_4F_2$ and the spectra of $O_2F_2$ and $O_3F_2$, it was unlikely that the paramagnetic species in $O_4F_2$ was the $O_2F\cdot$ radical.

The EPR spectrum of $O_3F_2$ at 90°K has also been investigated by Maguire (11). A doublet with a splitting of 13.6 gauss and a g-value of 1.975 was obtained. These results have been interpreted in terms of diradical $O_3F_2$ being the paramagnetic species involved. One unpaired electron is thought to be localized near each of the fluorine nuclei. The coupling between the two fluorine nuclei is considered to be weak, or zero.

Considering the results of the above investigations (10,11), it is highly probable that the radical species present in photolyzed $OF_2$ is OF·, via the dissociation $OF_2 \xrightarrow{h\upsilon} OF\cdot + F\cdot$ . However, we cannot uniquely identify the number of oxygens on the radical at this time. $^{17}OF_2$ is being prepared to make possible a more unambiguous identification of the paramagnetic species in photolyzed liquid $OF_2$.

The kinetics of the photolysis suggested the following as possible reactions:

$$(1) \quad OF_2 \quad \xrightarrow[\text{chain}]{h\upsilon} \quad OF\cdot + F\cdot$$

$$(2) \quad 2\,F\cdot \quad \longrightarrow \quad F_2$$

$$(3) \quad OF\cdot + M \quad \xrightarrow{h\upsilon} \quad R$$

$$(4) \quad OF\cdot \quad \xrightarrow{h\upsilon} \quad R'$$

$$(5) \quad OF\cdot + N \quad \longrightarrow \quad R''$$

As the temperature is increased, the photolysis proceeds more rapidly. More energy is available to increase the rate of reaction (1). In addition, dependent upon the temperature, reaction (1) will also proceed (via a chain mechanism) in the absence of light. Hence, a continued increase in the rate of formation at 77°K after the lamp is extinguished is observed. Reaction (3) and/or reaction (4) are the photolytic decay schemes which compete with reaction (1) when the lamp is on. With the lamp off at 77°K, the rate of formation increases rapidly for a short while, then drops back to a lower rate. This behavior can be explained by the fact that reactions (3) and (4) are not operating in the absence of light. Other, slower, temperature dependent decay schemes may be operation, i.e., reaction (5).

At higher temperatures (87°K, 100°K, 105°K), the decay of the signal is slow in the absence of light. Finally, at 120°K, the signal decays more rapidly after photolysis. The rate of the decay reactions was both temperature and photolytically dependent.

Figure 3 shows that continued photolysis caused the signal to reach a very low level. Thus, there must be a critical concentration which allowed the decay processes to predominate over the formation reactions.

SUMMARY

        This study has established that oxygen difluoride dissociates photolyti-
cally into a paramagnetic species in which there is a hyperfine interaction between
the unpaired electron and one fluorine nucleus.  The photolytic rate of formation of
the radical species increased with temperature.  The behavior of the signal inten-
sity in the absence of light after photolysis was also temperature dependent.  The
kinetics have been interpreted in terms of photolytic formation and decay schemes.
The radical has been characterized by means of the EPR spectrum, but not identified.
However, the characteristics of the spectrum indicated that the radical was $OF\cdot$,
rather than a higher oxygenated species or $F\cdot$.

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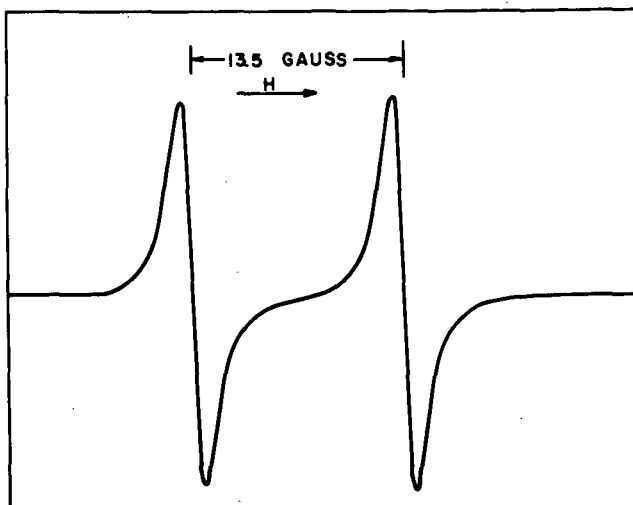
FIG.-1 EPR SPECTRUM OF LIQUID OF$_2$ AT 77°K
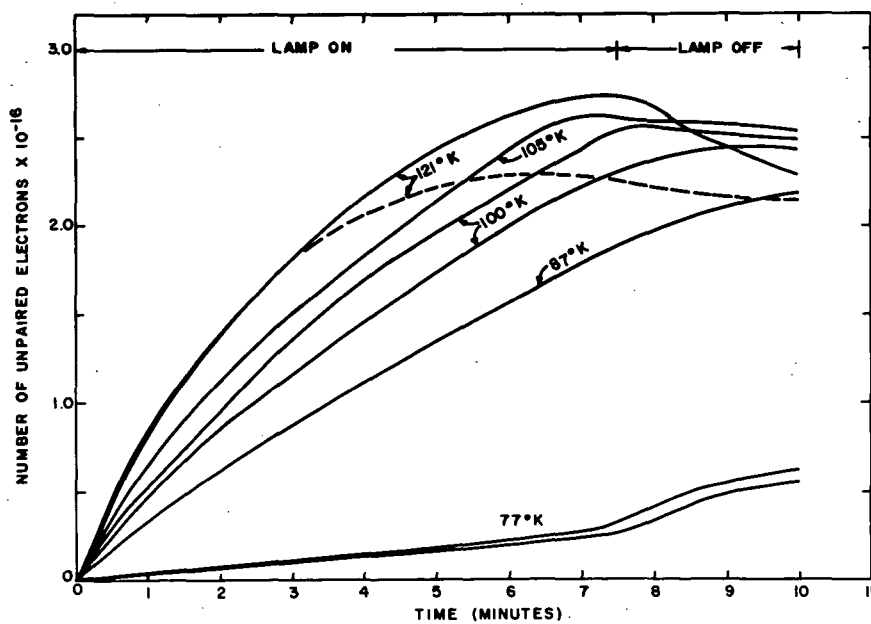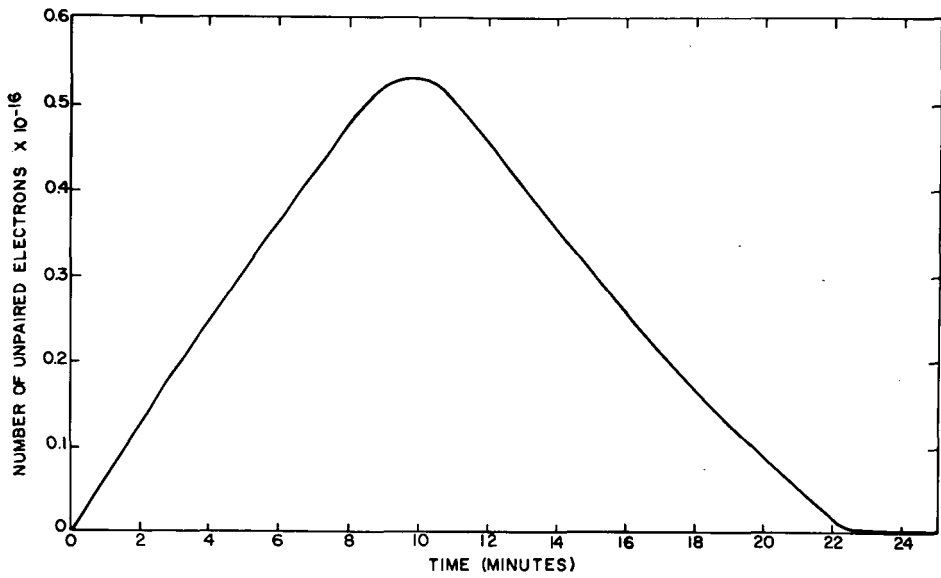


FIG.-2 PHOTOLYSIS OF LIQUID OF$_2$ AS A FUNCTION OF TEMPERATURE

FIG.-3 CONTINUED PHOTOLYSIS OF LIQUID $OF_2$ AT 77°K